CENTER FOR LOW-GRAVITY FLUID MECHANICS AND TRANSPORT PHENOMENA

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D.R. Kassoy
R.L. Sani

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UNIVERSITY OF COLORADO

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SUMMARY

The Center for Low-Gravity Fluid Mechanics and Transport Phenomena was initiated to develop a comprehensive program for research, education and outreach at the University of Colorado in support of the mission of the Microgravity Science and Applications Division of NASA. At the end of its NASA base funding period, the Center had evolved to a multidisciplinary organization involving twenty-two faculty members, postdoctoral researchers and graduate students in Center research and teaching activities. Two established low-gravity courses, the development of a third, and a weekly seminar series exemplified the Center's educational commitment. Extensive interactions were developed with representatives of the national and international low-gravity community.

I. INTRODUCTION

The Center for Low-Gravity Fluid Mechanics and Transport Phenomena began operation on September 1, 1986 with primary funding from the Microgravity Science and Applications Division of the Office of Space Science and Applications and additional matching funds from the University of Colorado. The program was designed to initiate new and unique activities in low-gravity science and engineering as part of the University of Colorado commitment to national leadership in space research. Participants were chosen from among faculty in the College of Engineering and elsewhere in the University on the basis of demonstrated technical excellence in fields with immediate impact on low-gravity fluid mechanics, heat and mass transport, combustion and related areas. A major goal of this group was to provide technical leadership in these areas. ["A Proposal to NASA, Office of Space Science and Applications for a Center for Low-Gravity Fluid Mechanics and Transport Phenomena." University of Colorado, CU Proposal # 0286.08.0159B, D.R. Kassoy and R.L. Sani].

The Center program focused on three primary activity areas:

* Research
* Education
* Outreach

During our funding period, significant progress was made in each of these areas, as documented in our progress reports. The program administrators, Professors D.R. Kassoy and R.L. Sani, developed management strategies for rapid spinup of quality low-gravity research programs. Internal proposals written by program participants to allow a reorientation of part of their research to the

low-gravity area were evaluated for technical effectiveness and merit. Support for faculty, graduate students, equipment and computer resources were provided from NASA and University funds. In addition, several postdoctoral researchers, chosen for excellence of achievement at the Ph.D. level, were integrated into the research programs. Many short and long-term research visitors provided additional technical expertise and breadth of interest. Noteworthy accomplishments in the research area include:

- o development of a national and an international visibility in microgravity science
- o ten low-gravity research projects involving nine faculty members, ten students and three postdoctoral researchers
- o one long-term and three short-term research visitors
- o technical presentations at professional meetings and at our Low-Gravity Sciences Day
- o collaborative projects with industrial, academic and government scientists in the low-g area
- o collaborative projects with European scientists

The Associate Director of our program, Professor Jean Koster played an important role in the development of our instructional activities. He designed and taught two courses specific to low-gravity sciences and technology. Specific accomplishments related to our educational mission include:

- o courses in low-gravity fluid mechanics and low-gravity material processing
- o thirty-five undergraduate and thirty-one graduate students have been enrolled in our low-gravity courses and seven students in independent study during our initial funding period
- o weekly seminars featuring external speakers who are actively involved in microgravity research at academic, industrial, and governmental institutions
- o development of a new course in mass transfer that specifically considers effects of a low-gravity environment by Professor Sani

Our Low-Gravity Science Seminar Series, a weekly series of lectures, supported by University of Colorado matching funds and given by representatives of the world-wide community involved with low-gravity activities was created to support both the research and educational missions of the Center. Speakers include scientists, engineers, astronauts and program administrators. This important activity provides research information exchange, educational benefits to our faculty and student participants as well as a forum which provided our participants with outside contacts for potential collaborative research.

The Center management team and other program participants fostered important outreach activities that include the development of cooperative research and educational programs with industry, government, laboratory and university groups, as well as providing expertise and knowledge of low-gravity sciences to external agencies, organizations and to the public. A particularly strong effort was made to draw the attention of the international low-gravity community to the activities of the Center. Primary accomplishments in the area of outreach include:

- o formal participatory agreements with individuals from 28 organizations
- o initiation of dialogue as well as cooperative research activities with two industrial partners and three NASA centers
- o initiation of dialogue as well as collaborative microgravity research activities with European and Chinese scientists fostered by ESA and the Chinese Academy of Sciences
- o technical session organization and presentations at meetings on space-related issues
- o publication of general interest and technical survey articles

A detailed description of these activities can be found in the Progress Reports submitted during the Center's NASA funding period.

II. CENTER RESEARCH ACTIVITIES

At the time MSAD/NASA base funding was terminated, the Center had developed an institutional structure for organizing and promoting a multi-disciplinary research and educational program in low-gravity fluid mechanics and transport phenomena. Outreach activities to the industrial community, to government laboratories, and to other universities were being emphasized in order to initiate new cooperative programs of mutual interest. Also a concerted effort was underway to develop more links with research groups in NASA centers where Center personnel's modeling and analysis expertise could be used to enhance the design of experiments and to improve the understanding of experimental data. Currently, for example, Center members provide technical support for joint projects at NASA Marshall Space Flight Center, NASA Lewis Research Center, CNES and CNRS (France). There was also an effort being initiated to coordinate our activities with, as well as provide modeling expertise to, two other NASA-funded Centers at the University of Colorado, the Center for Space Structures and Controls and the Bioserve Space Technologies Center. The former would be in the fluid handling area and the latter in the biofluid mechanics area, expertise areas of certain Center participants.

(A) Research

1. *General*

The Center seeded the development of ten low-gravity research programs involving participation by eight faculty members and twelve students:

1. Modeling of Microgravity Processing of Bimetallic Composite Materials
   R.H. Davis - Chemical Engineering

2. Thermomechanically Induced Convection in Helium
   D.R. Kassoy - Mechanical Engineering

3. Computer Aided Analysis of Flow and Transport in and Stability of Systems with Free and/or Moving Interfaces; Part 1: Floating Zones
   R.L. Sani - Chemical Engineering

4. Modeling Studies of Fluid Microstructural Effects of Relevance to Low-Gravity Materials Processing
   W.B. Krantz - Chemical Engineering

5. Flow and Transport in Binary Fluid Mixtures with Significant Soret Effect
   R.L. Sani - Chemical Engineering

6. Model Problems and Experiments on Fluid Systems with G-Jitter
   P.D. Weidman - Mechanical Engineering
   S. Biringen - Aerospace Engineering

7. Rapid Solidification of Undercooled Melts
   D.R. Kassoy - Mechanical Engineering

8. Electromagnetic-Capillary Instabilities of a Hollow Liquid Cylinder: Production of Spherical Shells Under Microgravity Conditions
   C.Y. Chow - Aerospace Engineering

9. Experiments on Low Prandtl Number Convection
   J.E. Hart - Astrophysical, Planetary and Atmospheric Sciences

10. Mass Transport in Vapor Phase Systems
    D.R. Kassoy - Mechanical Engineering

These research projects were an integral part of the Center's teaching function and have and will lead to the development of scientists with a unique background and understanding of microgravity science and engineering. It is noteworthy that these projects, originally created to redirect a fraction of the research of the Center's participants into the low-g area have, in many cases, been driven naturally into relevant low-g areas by interaction with visiting scientists and external contacts. This is evident from a perusal of the four newer projects in the next section. Some of these programs have developed

independent financial support from external agencies and from industrial sources. The leverage gained from our OSSA-NASA base funding allowed us to broaden and strengthen our micro-gravity research activities while providing OSSA-NASA with a very cost effective program of research and structure for the development of professionals in microgravity science. Currently, for example, as OSSA-NASA opts to discontinue base funding of the Center, Center participants have generated external research funding of approximately $850,000 in low-gravity and related areas from ARO, NSF, NATO, NASA, ONR and NOAA. Moreover Center participants have had or have ongoing collaborative research projects with personnel at three NASA centers (Marshall, Lewis and JPL), two industrial laboratories (Rockwell International Science Center, Photo Catalytics), foreign microgravity scientists representing CNES and CNRS (France), ESA (Germany, Spain and France) and the Chinese Academy of Science and numerous colleagues in academia. Brief descriptions of these and other research activities as well as accomplishments of both Center and external participants for each project are contained in the Center's previously submitted progress reports. In the next section, a more detailed description of four of the newer projects is presented to further illustrate the type and scientific merit of projects which were initiated during our base funding period.

Our postdoctoral researchers: A. Herczynski, Ph.D. in Applied Mathematics, Lehigh University, May 1987; S. Yiantsios, Ph.D. in Chemical Engineering, University of California at Davis, January 1989, and N.A. Hill, Ph.D. in Applied Mathematics, Imperial College, London, June 1985, will continue to support several of the projects described above as well as contribute to new and unique efforts resulting from interactions with external groups. In addition, Dr. E. Crespo del Arco, a visiting professor, financed by a grant from the Spanish government, initiated an ongoing collaborative project with Professor Sani on the modeling of thermocapillary flows during her visit.

Professor J. Koster, in his capacity of Assistant Professor of Aerospace Engineering Sciences developed an optical diagnostics laboratory facility for instructional and research activities, a facility which also should be useful as ground-based support equipment for the design of Professor Koster's IML-2 flight experiment. The Center management has allocated University of Colorado matching funds for equipment specific to this low-gravity mission. An effort has been made not to duplicate experimental research facilities available at NASA centers which our research programs would plan on using in place.

Our research activities at the end of our OSSA-NASA contract were evolving toward stronger interactions with programs at NASA centers, at other universities and in industry. A concerted effort was made since the inception of the Center to foster such collaborative projects. Initially such efforts experienced a great deal of resistance, due to the newness of the Center, and also due to the necessity to make the appropriate contacts in the microgravity science community. However, as is evident in the Center's Annual Progress Reports, our efforts have paid dividends. Our University-funded low-gravity science seminar series on low-g phenomena provided an excellent forum to initiate the necessary contacts and information exchange to foster such collaborative projects, another example of the leveraging of our NASA base funding which had evolved to a well-attended multi-disciplinary activity.

(B) Instruction

Center personnel created and offered undergraduate and graduate courses in many aspects of low-gravity sciences. These instructional programs, along with the weekly Low-Gravity Seminar Series, provided the basic educational material required by our participating graduate students. In addition, they attract a student body from the Aerospace, Chemical and Mechanical Engineering Departments interested in pursuing a career in space sciences and engineering as well as industrial people.

During our initial NASA grant period, the Center provided support for 16 graduate students, three postdoctoral research associates, and three visiting professors to perform research in the low-gravity area. Four of these students have received a Ph.D. degree; one of the postdoctoral research associates has taken a position with MSAD/NASA. With the growing focus on space research at the University of Colorado, we had anticipated an even larger output in the future.

III. CLOSING REMARKS

During its NASA grant, the Center evolved into an effective and efficient resource for both the national and international microgravity science community and MSAD mission in general. The Center developed an effective multidisciplinary organizational structure for not only research but also the education of microgravity-science-oriented scientists and engineers. The embedding of the Center as an umbrella organization within the College of Engineering and Applied Science at the University of Colorado as well as reorienting and utilizing the expertise of established College researchers as Center participants aided in the development, the effectiveness and the minimal administrative cost of the Center. The Center provided an effective structure for leverage of University and NASA resources for education and research in the multidisciplinary area of microgravity sciences, an effectiveness which is difficult to achieve and sustain by individual research grants.

2. *Details of Four of the Newer Research Projects*

A. MASS TRANSPORT IN VAPOR PHASE SYSTEMS

D.R. Kassoy, Professor, Department of Mechanical Engineering
A. Herczynski, Research Associate, CLgFT
B. Zappoli, CNES, France

A.1. Introduction

The results of the Chemical Vapor Transport (CVT) and Physical Vapor Transport (PVT) experiments in space have caused considerable concern within the microgravity community in recent years. These experiments, aimed at obtaining an ideal crystal-growing facility where one could generate single crystals of high quality, have confronted researchers with unexpected fluid dynamics phenomena, the understanding of which is necessary before further progress in this area will be possible.

The principal idea behind CVT and PVT experiments is to have a closed ampoule with the polycrystaline material removed by a chemical reaction or sublimating at the hotter end and recrystalizing in a controlled manner at the cold end of the ampoule. The transfer of the vapor from one side of the ampoule to another occurs with the help of a carrier gas whose pressure can be suitably adjusted.

In the case of PVT the carrier gas is neutral and inert. In CVT, the transport gas reacts with the crystalline material at the hotter end, and the resulting compound undergoes a reverse reaction at the colder end. Crystalline materials typically used in CVT are *GeS*, *GeSe*, *GeTe*, $GeS_{.98}Te_{.01}$, while typical carrier gases are $GeCl_4$ and GeI_4 (see, for example Sperry and Yoel[1]). Such systems can involve multiple chemical reactions, not only at the interfaces but also in the bulk vapor phase.

In ground-based experiments the efforts to obtain good quality crystals using CVT methods have been frustrated by the preeminence of natural convection which is the main cause of irregularities in the crystal lattice. It therefore seems desirable to conduct CVT and PVT experiments in a reduced gravity environment in order to achieve a diffusion-controlled process and thus more regular crystals.

However, not only the quality of crystals grown in space has often been disappointing, but the mass flux rates themselves have proved to be unpredictable and, in certain cases, much larger than expected. It has been reported by Wiedemeier and his collaborators[2,3] that CVT experiments in space involving *GeSe* show fluxes in excess of 400% of the rates predicted by pure diffusion. Similar startling results have been obtained in other experiments[1,4,5]. Furthermore, a fluctuation in the bulk temperature has been observed, most likely due to chemical reaction in the vapor phase. The discrepancy between the predicted and the observed flux rates clearly indicates that another mechanism for driving the fluid motion is present and unaccounted for in the existing modeling.

It is probable that the large fluxes arise from the low Mach number compressibility effects in the gases. When the real gas is heated, either at the boundary of the container or in bulk, it responds on the local level by thermal expansion of small fluid parcels whose temperatures are rising. This expansion induces bulk motion and, if the heating is rapid enough, a mechanical disturbance propagating through the fluid in the form of an acoustic wave. Particularly in the case of an unsteady heat release this thermomechanical process may result in very significant fluid motion[6]. In addition, the effects of heat conduction change the state of the gas on a longer time scale and, in turn, alter the motion.

Thermomechanical effects clearly play a role in mass transfer in CVT systems. Even in the absence of the volumetric heat release due to a homogeneous reaction, the endothermic and exothermic reactions at the source and crystal ends, respectively, may affect the system. If, in addition, bulk transient heating is present, this mechanism can provide a driving force which will

alter the results of mass diffusion due to concentration gradients. Thus, in order to be able to predict correctly mass transfer rates in the closed CVT systems, the compressibility effects have to be included in the analysis of the gas motion.

A.2. Purpose of the Study

The main purpose of the proposed study is to model thermally generated transient bulk motion in microgravity systems in order to understand the fluid dynamics of CVT and PVT experiments. While considerable attention has been given in recent years to other physical mechanisms that drive non-buoyant convection in fluids (e.g. Marangoni effects in reduced gravity), little is known about the mass motion induced by transient heating in systems with no surface forces and no natural convection.

The practical importance of thermocapillary forces in liquid-gas systems is long established, particularly in the floating-zone configuration. On the other hand, it has become increasingly clear that any mechanism contributing to the bulk motion of the vapor must play a crucial role in CVT and PVT experiments in space. Thus, for proper understanding of the fluid dynamical processes involved in these experiments it is necessary to develop models of gas flow generated by localized transient thermal expansion in closed systems.

Existing CVT literature considers mass fluxes in vapor deposition experiments in terms of diffusion-limited processes. This approach does not take into account compressibilty effects in the gas, and fails to predict observed mass motion within CVT ampoules at nearly zero-gravity. For this reason, we propose to analyze the vapor transport experiments by taking into consideration both mass diffusion due to concentration gradients and mass flux resulting from thermomechanical response of vapor gas to unsteady heating in the system. Such analysis can be carried out by constructing simplified, mathematical models extracting the salient features of the system.

Because CVT experiments involve complicated, multicomponent systems with several chemical reactions occurring within the closed ampoule, it is desirable to consider several subproblems separately. We plan to construct a series of models that incorporate increasingly complex physical and chemical mechanisms found in experimental systems. We can thus study the relative importance of fluid dynamical phenomena that occur in vapor transport systems.

For modeling purposes internal volumetric heating (e.g. due to a chemical reaction in the vapor phase) and heating at boundaries of the system need to be distinguished. Different models are obtained depending on whether the heating variations occur on an acoustic or longer time scale. For some modes of heat addition (particularly when power deposition is at the wall, or volume heating is on an acoustic time scale) acoustic waves are generated in the gas. These waves, propagating through the medium, may affect internal heat transfer and, especially, the coupled mass and heat transfer at the boundaries corresponding to interfaces at the ends of the ampoule. The significance of these phenomena will be investigated within the framework of the mathematical analysis.

In order to closely approximate the fluid dynamical processes of CVT and PVT systems, the bulk and boundary heating must be included in such a way that it reflects the observed features of the real systems. In the case of CVT the volume heat release should correspond to any reaction in the chemical system. In both cases the thermal effects of the processes at the interfaces must be included in the analysis. This means including in the modeling endothermic sublimation and exothermic crystalization for PVT, and the latent heat of reaction and reverse reaction for CVT. Then the effects of these processes on the bulk mass transfer, and ultimately, the quality of the grown crystal can be assessed.

A.3. Problem Formulation

Initially one-dimensional continuum models of the fundamental physics will be used to investigate the basic thermo-mechanical effects without the complications that may arise from more realistic geometry. This simplification means essentially that in our initial model the effect of gas viscosity near the ampoule walls will not be included. That this effect may be significant, particularly in the case of zero-gravity, has been shown by Greenwell *et al*[7]. Nevertheless, it is first necessary to understand the role thermo-mechanical phenomena play in a one-dimensional system before two-dimensional effects can be included in analysis.

In order to obtain the most general formulation, readily applicable to particular systems, the model is first cast in terms of general, nondimensional equations. The spatial variable is rendered nondimensional by the use of characteristic size (length) of the system. Following the earlier work on thermoacoustical response of the gas to heating in the absence of gravity by Kassoy[8] and Radhwan and Kassoy[6], the nondimensionalization of the time variable is with respect to acoustic time, and the velocity variable with respect to speed of sound. In this formulation, the relative importance of each of the terms in momentum and energy equation can be easily judged. The perturbation methods are then used to obtain a simpler set of equations, describing the dominant physical features of the system. The small parameter, on which the scaling of the variables and asymptotic expansion is based, depends on magnitude and characteristic time of the heating function.

We will assume an ideal gas equation of state for the carrier gas whether inert or not, as well as for the second species (vapor), if present. Due to exclusion of the gravity, the momentum equation in all models will have a simple form, with no external body force. The form of the energy equation depends on whether volume heating is present or not. When internal heating is present, the heat source term will be written as a product of two functions, one describing the spatial dependence and the other temporal dependence of the released heat. The temporal part may have an oscillatory form, to mimic oscillations observed in CVT experiments. In addition to the above-mentioned equations a species equation is included in the models considering diffusive processes in the mixture of gases.

To complete the model, appropriate initial and boundary conditions have to be specified. We will assume that initially only one gas is present in the closed container and that the system is at rest and in thermodynamic equilibrium. Thus the velocity and acceleration are zero everywhere at $t = 0$. The temperatures at the two boundaries are constant and unequal, as is the case in vapor transport systems. Even though the model is one-dimensional, it will allow for an arbitrary initial temperature profile (corresponding to an oven profile in experiment) within the system, with the specified values at the ends. The boundary conditions will require that the carrier gas is always at rest at the ends. For the case of two gases present in the PVT system, boundary conditions must specify the mass transfer rates of the second gas across the walls, corresponding to sublimation (gas enters the container) at the hotter end, and crystalization (gas is removed from the container) at the colder end. In addition to these conditions, a model must include thermal boundary conditions describing the endo- and exothermic characteristics of the sublimation and crystalization, respectively, which tend to offset the temperature gradient. In the case of CVT, the thermal effects of reaction at the hotter end and reverse reaction at the colder end will be included in the boundary conditions.

A.4. Current Status of Research

The perturbation approach to problems concerning thermomechanical processes in compressible fluids hinges on a careful introduction of the appropriate time scales for the involved phenomena. The distinction between acoustic-time and conduction-time phenomena was first utilized for the mathematical analysis of these problems by Kassoy in the previously mentioned paper on the response of a confined gas to a thermal disturbance[8]. In this work, matched asymptotic expansion solution is first developed for the short acoustic time, and multiple scale analysis is

employed for the longer conduction times. This approach, which properly resolves the physical mechanisms involved, has been extended by Radhwan and Kassoy[6] and applied by Sutrisno and Kassoy[9] to the problem of helium gas heated at the boundary of a slot between two planes.

The response of a confined gas to volume heating is currently being addressed and the analysis of the mass transport in a one-dimensional system is being completed and prepared for the publication[10]. In this work the exact conditions under which a unidirectional mass flux occurs in the system are predicted and the effects of various volume heating functions are investigated. In addition to considering the volume heating function with the temporal variation occurring on a long time scale, corresponding to observed temperature oscillations in CVT experiments, a separate model is being considered for the heat addition occurring on the acoustic time scale.

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B. DROPLET COLLISIONS AND COALESCENCE IN MICROGRAVITY

R.H. Davis, Associate Professor, Department of Chemical Engineering
N.A. Hill, Postdoctoral Research Associate, CLgFT
S. Yiantsios, Postdoctoral Research Associate, CLgFT
J.R. Rogers, Graduate Student, Department of Chemical Engineering
X. Zhang, Graduate Student, Department of Chemical Engineering
D.O. Frazier, NASA Marshall Space Flight Center
E.H. Trinh, Jet Propulsion Laboratory

B.1. Introduction

Collisions and coalescence of liquid drops play key roles in a variety of natural and industrial processes, such as rain drop formation, liquid-liquid extraction, and the formation of composite materials from liquid phase miscibility gap metals. Unfortunately, these phenomena are very complicated and are poorly understood to date. For example, Van Alstine[1] observed very rapid coalescence and phase segregation of two immiscible aqueous polymer phases during KC-135 microgravity conditions, whereas Lacy and Otto[2] observed a dramatic reduction in the rate of coalescence of Krytox oil in water when subjected to the low-gravity environment of the Skylab 4 mission. Seemingly disparate observations such as these need to be understood on a comprehensive and rational scientific basis.

Previous ground-based and microgravity research on droplet coalescence has primarily involved two classes of dispersions: liquid phase miscibility gap (LPMG) metals and transparent immiscible liquids. There has been considerable experimental work in producing LPMG composite materials under low-gravity conditions[3-8]. The general procedure for producing immiscible alloys is to heat the desired composition of the two metals to a temperature corresponding to the single phase liquid above the miscibility gap and then to cool the mixture either naturally or by controlled gradient or isothermal methods. As the mixture cools through the miscibility gap, droplets rich in one metal form in a matrix of a second liquid phase rich in the other metal. The hope is that the matrix will solidify before any significant droplet phase segregation occurs.

Lacy and Otto[3] reported on early drop tower experiments with Ga-Bi that clearly showed finer and more homogeneous dispersions of Ga particles in the Bi matrix for the free-fall solidified samples as compared to a normal gravity sample processed under otherwise identical conditions. Unfortunately, this success appears to be the exception rather than the rule[4]. Carlberg and Fredriksson[5,6] discussed TEXUS sounding rocket experiments with Zn-Bi LPMG immiscible alloys. For dilute systems (8% or less Bi), homogeneous dispersions were found, but with Bi droplets larger than expected from diffusion-controlled growth, indicating that collision-coalescence had occurred. In samples with higher Bi content, large regions of the Bi-rich phase appeared in the interior of the samples and in layers surrounding the samples, the latter indicating a preferential wetting of the container wall. Walter[7] also reported that uniform dispersions could only be obtained at dilute volume fractions (<10%) of the dispersed phase.

The other class of relevant experiments includes model transparent systems of two non-metallic immiscible liquids[1,9-13]. Such experiments are very useful, as they can monitor (by microphotography, holography, and other optical techniques) droplet motion, droplet interaction and coalescence, and changes in the size distribution of the dispersed phases with respect to time. This is a distinct advantage over the use of opaque systems (such as metals) for which only the final composite structure can be analyzed. Caution must be used in applying the results of studies with model transparent systems, however, since their physical properties and dominant mechanisms may be very different than those of metals.

A variety of mechanisms have been proposed in the scientific literature as the causes of droplet and particle motion, coalescence, agglomeration and phase segregation during the cooling of liquid phase miscibility gap and other bi-metallic composite materials. Theoretical estimates of the magnitudes of different mechanisms in specific systems have led to the conclusion that thermocapillary or Marangoni motion of droplets, followed by droplet collision and coalescence or segregation in a common area of the sample, is the likely dominant mechanism under microgravity processing conditions[6]. However, Brownian motion may be the dominant mechanism for very small droplets or in the absence of a temperature gradient, and gravity sedimentation usually (but not always) dominates for ground-based processes.

Although considerable effort has been undertaken to study coalescence and phase segregation in miscible liquids processed in microgravity, it is clear that further experiments and modeling are needed in order to understand the basic phenomena and to develop predictive capabilities for coalescence and segregations rates. In particular, an assessment of the state-of-the-art reveals the need for advanced modeling efforts on the mechanics of droplet interactions and for experiments performed under carefully controlled conditions.

B.2. Objectives and Significance of the Study

B.2.1 Objectives of Research Project

The overall objective of the research project is to examine and understand the kinetics of the coarsening process due to droplet collisions and coalescence in immiscible liquid-liquid dispersions, both in the absence and in the presence of gravity. The specific objectives are to use theoretical modelling and ground-based and low-gravity experiments to assess the individual and collective roles of Brownian motion, Marangoni migration, and gravity sedimentation on promoting coalescence, and to compare the measured rates of shift of the droplet size distributions to simulations using population dynamics models. A specific hypothesis to be tested is that different mechanisms for relative droplet motion dominate the coalescence process for different parameter ranges. For example, it is expected that Brownian motion is most important for very small drops or in the absence of temperature gradients and gravity, and that Marangoni motion and gravity sedimentation are most important for larger drops in the presence of a temperature gradient or gravitation field, respectively.

B.2.2 Significance of Research Project

The primary significance of the program is that it will yield important quantitative information on the poorly understood phenomenon of coalescence. In particular, the relative importance of various mechanisms in promoting coalescence will be delineated by the proposed theory and experiments. The insight gained in this fundamental research will have practical application in important processes such as liquid phase miscibility gap (LPMG) bimetallic composite materials processing and biological separations using aqueous two-phase extraction. In addition, the theoretical and experimental methods being developed for following droplet collisions and size distributions are expected to serve as tools for a variety of uses involving transparent materials.

B.2.3 Relevance of Research Program to Microgravity Science

The research program encompasses an area where the low-gravity environment is an important tool both for providing a better understanding of the role of gravity in Earth-based processes and for providing processing capabilities that are unique to the low-gravity environment. For example, since the densities of two transparent immiscible liquids may be matched, in general, only at a single temperature, it is not possible to study droplet coalescence due to thermal Marangoni migration in the complete absence of gravity sedimentation effects on Earth. Moreover, a density match at any temperature is generally not possible when studying prespecified materials of commercial value such as immiscible metal alloys or aqueous two-phase extraction systems.

B.3 Research Formulation and Approach

The research program involves both modelling and experiment. Each of these has two components: A macroscopic phenomena component that studies shifts in droplet size distributions and phase segregation with time during low-gravity processing of immiscible fluids, and a microscopic phenomena component that studies the collision and coalescence of two interacting droplets. These two components are intimately coupled, since it is the mechanics of the microscopic phenomena that determine that rate at which the macroscopic phenomena occur.

The theoretical research is being undertaken in the Center for Low-Gravity Fluid Mechanics and Transport Phenomena at the University of Colorado in Boulder, under the direction of Professor Robert H. Davis. The experimental research is being undertaken in collaboration with Don Frazier at NASA Marshall and with Eugene Trinh at the Jet Propulsion Laboratory. The macroscopic and microscopic components are described below.

B.3.1 Macroscopic Phenomena

Theory

The theoretical portion of the macroscopic phenomena component of this project is being performed at the Center for Low-Gravity Fluid Mechanics and Transport Phenomena at the University of Colorado in Boulder. It is directed by Professor Robert H. Davis, and performed with the aid of a Postdoctoral Research Associate, Nick Hill, and a graduate student, Jan Rogers.

The primary objective of the theoretical research is to develop and solve population dynamics models in order to predict the evolution of the droplet size distribution with time due to collisions and coalescence under the individual and collective action of Brownian motion, Marangoni migration, and gravity sedimentation. The primary significance of this research is that the predicted rates of droplet growth may be used to design the experiments and then be quantitatively compared to the measurements.

Thermocapillary migration (alternately referred to as thermal Marangoni motion) of bubbles and droplets through a liquid occurs in the presence of a temperature gradient and is caused by a variation in interfacial tension brought about by the temperature gradient. This variation causes a surface force on the bubble or droplet so that it migrates in the direction of the lowest surface tension. In general, this corresponds to the direction of higher temperature. A similar migration, known as solutal Marangoni motion, occurs in the presence of a concentration gradient of a solute which influences the interfacial tension.

Thermocapillary migration of bubbles was first demonstrated by Young et al[14], who also derived an expression for the drop migration velocity, valid for droplets sufficiently small that heat and momentum transport convective contributions may be neglected:

$$\vec{U}_m = \frac{2}{(2+k^*)(2+3\eta^*)} \frac{a}{\eta} \left(-\frac{\partial \gamma}{\partial T}\right) \nabla T_\infty \qquad (1)$$

where ∇T_∞ is the undisturbed temperature gradient (assumed uniform over a scale large compared to the droplets radius, a), γ is the interfacial tension, η is the surrounding liquid viscosity, and k^* and η^* are the ratios of the thermal conductivities and viscosities, respectively, between internal and surrounding fluids. Equation (1) is valid only in the limit as the Marangoni number, $\mathrm{Ma} = aU_m/\alpha$, and the Reynolds number, $\mathrm{Re} = U_m a/\nu$, approach zero, where α and ν are the thermal diffusivity and the kinematic viscosity of the continuous phase, respectively. More recent fundamental theoretical work on thermocapillary migration by Subramanian at Clarkson, and others, includes larger Reynolds and Marangoni numbers and interactions between two droplets or bubbles or between a bubble and a plane[15-17].

Stokes sedimentation of particles due to residual gravity is governed by Hadamard's relationship[18]:

$$\bar{U}_s = \frac{2}{3}\frac{a^2}{\eta}\frac{(\eta^* + 1)}{(3\eta^* + 2)}(\rho - \rho')\bar{g} \tag{2}$$

where $\bar{g}$ is the residual gravity vector and $\rho - \rho'$ is the density difference between the droplet and continuous phases. Droplets with different radii will move at different Stokes velocities and thus have the potential to collide and coalesce.

The general population balance equation that is used in the macroscopic model is described by Rogers and Davis[19]

$$\frac{\partial n_j}{\partial t} = \frac{1}{2}\sum_{j=1}^{i-1} J(V_i, V_{j-1}) - \sum_{i=1}^{\infty} J(V_i, V_j) \tag{3}$$

where n_j is the number of droplets of volume V_j, per unit volume, and $J(V_i, V_j)$ is the rate of collisions resulting in coalescence (number of collisions per time per unit volume) of droplets of volume V_i with droplet of volume V_j. The first term in the right-hand side of (3) represents the formation of droplets of volume V_j due to coalescence of two small drops (the factor of 1/2 prevents double counting), and the second term represents the destruction of drops of volume V_j due to coalescence with other drops.

Expressions for the collision rates for individual mechanisms may be developed using the classic work of Smoluchowski[20] for colloidal particles:

Brownian Collisions $$J(V_i, V_j) = 4\pi n_i n_j D_{ij}(a_i + a_j)E_{ij} \tag{4}$$

Marangoni Collisions $$J(V_i, V_j) = n_i n_j (U_{m,i} - U_{m,j})\pi(a_i + a_j)^2 E_{ij} \tag{5}$$

Stokes Collisions $$J(V_i, V_j) = n_i n_j (U_{s,i} - U_{s,j})\pi(a_i + a_j)^2 E_{ij} \tag{6}$$

where a_i and a_j are the radii of droplets of volume V_i and V_j, respectively, D_{ij} is the relative Brownian diffusivity of droplets of size i and size j undergoing independent Brownian motion, U_m and U_s are the magnitudes of the Marangoni and Stokes velocities given by (1) and (2), respectively, and E_{ij} is the collision efficiency. The relative diffusivity is given by the Stokes-Einstein equation:

$$D_{ij} = kT(b_i + b_j) \tag{7}$$

where b_i and b_j are the mobilities of drops of size i and size j, respectively. For rigid spheres, these are given by the well-known Stokes formula: $b = (6\pi\eta a)^{-1}$, whereas for fluid droplets they are

given by the lesser known Hadamard formula:

$$b = (2\pi a\eta(3\eta^* + 2)/(\eta^* + 1))^{-1} \tag{8}$$

Collision efficiencies of unity ($E_{ij} = 1$) result when it is assumed that the droplets do not interact prior to colliding. Values differing from unity (usually $E_{ij} < 1$) represent the influence of fluid dynamic and attractive or repulsive interactions between the droplets during their relative motion. Predictions of the collision efficiencies is a major task of the studies of microscopic phenomena.

Our approach is to implement the population dynamics model by first discretizing the initial size distribution using a log scale[19]. A time-stepping procedure is used to determine the new size distribution at each time step by solving (3) for each size category in order to determine the change in the number density of droplets in the category during the time step. Specific macroscopic modeling tasks are:

(i) Develop program to solve population dynamics model for gravity sedimentation (Stokes collisions) and Marangoni migration with collision efficiencies of unity (completed).

(ii) Develop program to solve population dynamics model for Brownian motion with collision efficiencies of unity.

(iii) Incorporate rigid-sphere collision efficiencies, including attractive van der Waals interactions, into population dynamics model for gravity sedimentation (completed).

(iv) Incorporate fluid-droplet collision efficiencies into population dynamics model for gravity sedimentation, Marangoni migration and Brownian motion.

(v) Develop population dynamics models for combined mechanisms.

(vi) Develop scaling laws and perform order-of-magnitude estimates of the rate of droplet growth due to the various mechanisms, as needed, to help specify the experiment design.

(vii) Solve population dynamics models in order to predict the time evolution of the droplet size distribution due to coalescence under the specific conditions of the experiments performed.

Experiment

The experimental portion of the macroscopic phenomena component of this project is being performed in collaboration with NASA Marshall Space Flight Center (MSFC). Ms. Jan Rogers is assisting with the experiments through the Graduate Student Researchers Program (GSRP). While at the Space Science Laboratory at MSFC, she is directed by Don Frazier, with assistance from Bill Witherow and Barbara Facemire.

The ground-based experiment program at MSFC includes the following tasks:

(i) Choosing appropriate immiscible liquid systems and measuring the required fluid properties.

(ii) Improving current holographic technology for measuring droplet size distributions.

(iii) Determining the minimum droplet size and the maximum droplet phase volume fraction measurable by holographic technology.

(iv) Designing the cell configuration and support apparatus required for ground-based and low-gravity coalescence experiments.

(v) Performing ground-based experiments to measure the evolution of droplet-size distributions with time due to droplet collisions and coalescence arising from Brownian motion, gravity sedimentation and Marangoni migration.

(vi) Modifying image analysis system for reconstructing holograms and analyzing experimental data.

The low-gravity experiment program has been proposed by Frazier and Davis[21] for the HOLIDDO apparatus on the IML-2 mission. The test cell will be loaded with an immiscible fluid mixture prior to flight. Mechanical stirring will be initiated at the start of the experiment in order to achieve a fine dispersion. The initial phase of the experiment will be isothermal so that the primary droplet growth mechanism is Brownian-induced coalescence. A thermal gradient will be applied after 10-20 hours so that the primary droplet growth mechanism during the second phase will be Marangoni-induced coalescence. Combined effects of Brownian motion and Marangoni migration will be observed in a second experiment. In all cases, holographic photography and analysis will be used to follow droplet-size distributions.

B.3.2 Microscopic Phenomena

Theory

The theoretical portion of the microscopic phenomena component of this project is being performed at the Center for Low-Gravity Fluid Mechanics and Transport Phenomena at the University of Colorado in Boulder. It is directed by Professor Robert H. Davis, and performed with the aid of a Postdoctoral Research Associate, Stergios Yiantsios, and a graduate student, Xiaoguang Zhang.

The primary objective of this research is to predict the conditions for coalescence, and the time for coalescence, of two drops in relative motion. This will allow for the determination of critical impact parameters and collision efficiencies that will be used in the population dynamics model. The tasks to be undertaken are as follows:

(i) **Two-sphere mobility functions for drops and bubbles.**

For low-Reynolds numbers, the velocities of two interacting sphere are linearly related to the applied forces. The coefficients known as mobility functions depend on the size ratio of the two spheres and on their separation[22]. Since these functions are necessary to compute the trajectories of two colliding drops or bubbles[23], the first problem will be to tabulate these functions. Although complete information is readily available for solid spheres[24], this is not the case for drops and bubbles.[25]

(ii) **Axisymmetric trajectory calculation for spherical drops and bubbles.**

The numerical procedure to be used is a time-stepping calculation of the relative velocity of two droplets or bubbles initially placed at a distance apart, and driven together by specified applied forces (gravity, thermocapillary, acoustic, or van der Waals). The distance travelled during the time step is then calculated. The calculation is continued until the fluid particles come into contact and coalesce, or come to rest at a finite distance apart.

(iii) **Non-axisymmetric trajectory calculations.**

The procedure described by Davis[23] will be used for the case when the motion is not along the line of centers. It will be assumed that the forces on the bubbles act in a parallel direction (a restriction that may be relaxed later), so that the particles move in a parallel direction when they are

sufficiently far apart. Trajectories will be computed for varying impact parameters. The critical impact parameter which will just allow contact will be determined as a function of the size and viscosity ratios and of the applied force. The collision efficiency will then be determined from the critical impact parameter.

(iv) **Film drainage and deformation of drops and bubbles in near contact.**

This task will address the problem dealing with the effect of the drop deformation on the probability for coalescence as well as on the coalescence time. The near-contact relative motion of deformable droplets will be studied using the techniques developed by Davis and co-workers[26] for spherical drops. The extension to nonspherical drops will be made by using the normal stress balance on the drop surface. In particular, film drainage in the narrow gap will be described by lubrication theory, and the flow inside the drop will be analyzed using the boundary integral formulation of the Stokes equations. These two flows are coupled as the result of the non-zero tangential velocity and stresses at the interface, and they must be determined simultaneously. The proposed theory represents a significant improvement over earlier film drainage treatments[27] which only solved for the decoupled flow in the film by assuming either that the interface was either immobile, stress-free, or governed by an interfacial viscosity.

A time-stepping procedure will again be used where upgraded velocity, pressure, and deformed gap thickness profiles will be determined at each time step. Dr. Davis has already developed sophisticated numerical codes to perform such a procedure for the analogous problem of film drainage between two elastic particles in close approach[28]. In addition, a normal mode stability analysis will be performed in order to examine the role of van der Waals attractive force on the film rupture and coalescence[27]. Coalescence times will be computed for the ranges of size and viscosity ratios, interfacial tension, and Hamaker constant (magnitude of van der Waals attraction) relevant to the proposed ground-based and microgravity experiments.

Experiment

The experimental portion of the microscopic phenomena component of this project will be performed at the Jet Propulsion Laboratory in collaboration with Eugene Trinh and co-workers. An ultrasonic cell of the type used previously to study droplet oscillations[29] will be used to study the relative motion and coalescence of two drops. Microgravity experiments are proposed for the Bubble, Drop and Particle Unit (BDPU) offered by ESA, or for a modified Drop Physics Module. The experimental tasks are described below.

(i) Ground-based studies will include high-speed video camera recording of the process of coalescence of two drops immersed in an immiscible liquid host with varying drop viscosity, drop relative velocity and size, impact parameter (including impact at an angle), drop-host interfacial tension, and surfactant contamination. The parameters measured will be the coalescence time and the deformation upon contact. The emphasis will be placed on the determination of the optimum optical configuration and lighting to visualize the interfacial film between the two colliding droplets, and the adaptation of these conditions to a flight experiment configuration. Additional required data will be the identification of the optimal host and drop liquids for the flight experiment to yield the most interesting and definitive results. The constraints inherent in a flight experiment address safety issues as well as the limited range for variation of physical parameters due to limited volume, power, and time availability.

(ii) Limited ground-based experiments will be carried out for bubble-bubble coalescence due to the large buoyancy force. The recording of the collision and coalescence process of a bubble rising towards an acoustically trapped second bubble will be done with different bubble sizes and liquid surface tension. The quantitative evaluation of the coalescence time will be required before the design of the space experiment. The use of surfactant may be required in order to slow the coalescence process. The size of the bubbles investigated in 1 g will range between 2 and 5 mm in diameter. The technique for manipulating two bubbles toward each other will also be perfected for a totally automated operation.

(iii) The flight experiment will primarily address the collision and coalescence of bubbles since this type of investigation cannot be carried out rigorously on Earth, although some microgravity experiments will still be performed with droplets. At least three cells containing different compositions of degassed water and glycerin mixtures with viscosity range between 1 and 50 cP will be used in combination with air and inert gas bubbles and silicone oil droplets. The variation of the interfacial tension will be implemented by using another cell filled with a hydrocarbon liquid or silicone oil. The following steps describe a generic experiment:

1. The experiments will typically start by the deployment of the appropriate pair of droplets or bubbles of small diameter (about 2 mm).

2. An in-situ measurement of the interfacial tension will then be carried out by measuring the frequency of the fundamental mode of driven shape oscillation carried out through the modulation of the carrier frequency at the appropriate lower frequency.

3. Video or cinefilm recording will provide the values of the radii of the two particles.

4. The appropriate change in the cell resonant mode will then bring the particles together, and the process of collision and coalescence will be recorded.

5. A new fluid particle will then be injected, and the same sequence repeated.

6. This same general type of experiment will be repeated in the presence of a known linear thermal gradient to measure the motion of two droplets or bubbles driven toward each other by force of thermocapillary origin.

In this manner, a combination of different sizes of particles could be investigated without having to withdraw the injected fluid. When an appropriate size of bubble has been obtained through coalescence, the same bubble can be used for the nonlinear bubble dynamics studies. A careful timelining of the three sets of different experiments will be required to minimize the change of the cells.

B.4 Current Status of Research

Considerable progress on theoretical modeling of the macroscopic phenomena of droplet growth due to collisions and coalescence has been made. Rogers and Davis[19,30] have submitted two papers describing their work on population balances to predict shifts in droplet size distributions due to gravity-induced and thermocapillary-induced coalescence. Similarly, significant progress on theoretical modelling of the microscopic phenomenon of interactions between two drops has been made. Davis and co-workers[26,31,32] have developed a novel analytical technique of combining lubrication theory and boundary integral methods to solve for the coupled flow in the droplet phase and in the host fluid.

The experimental studies have been planned but are not yet underway. The ground-based macroscopic phenomenon experiments will be initiated during February-June 1989 when Jan Rogers works at MSFC under the GSRP. Flight experiments to study the microscopic and macroscopic coalescence phenomena under low-gravity conditions have been proposed to NASA in response to AO OSSA-4-88 [21,33].

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C. RAPID SOLIDIFICATION OF UNDERCOOLED MELTS

D.R. Kassoy, Professor, Department of Mechanical Engineering
J.A. Norris, Graduate Student, Department of Mechanical Engineering

C.1. Introduction

Recent advances in materials processing have drawn attention to the development of materials, such as glassy metals, formed under non-equilibrium conditions. Forming these materials requires high cooling rates, as with splat cooling, and the ability to significantly undercool melts prior to solidification. The effective low gravity found in space eliminates the usual buoyancy induced convection. The resulting quiescent liquid is amenable to significant undercooling.

Under these circumstances, where systems are far from thermodynamic equilibrium, solidification phenomena are, currently, poorly understood. Traditional solidification modeling hides the important physics by looking at the problem on too large a scale. The goal of this research is to study solidification on a much smaller scale by examining the structure of the solidification zone. This will be accomplished by incorporating rate laws for nucleation kinetics and heat release into the governing continuum equations.

C.2. Background

Along with the changes in material properties, the heat of fusion is released during solidification. If the rate of release is sufficiently small, the heat will be transported away, otherwise, it may raise the local temperature, a process known as recalescence.

When a material is not in equilibrium, mass and heat diffusion drive the system toward equilibrium. These processes occur at different rates, typically with heat diffusion being the fastest, then mass diffusion in a liquid, and solid mass diffusion the slowest. For the slowest rates of solidification, there is sufficient time for diffusion processes to maintain global equilibrium. With faster solidification rates, global equilibrium is not maintained, although local equilibrium may still hold at the interface.

In most solidification modeling, the heat of fusion is assumed to be released instantaneously. This means that the time scale for heat release is much smaller than those of other transfer mechanisms. If mild undercooling is being modeled, it is often assumed that recalescence immediately raises the interface temperature to the equilibrium melting point. In addition, for pure materials with a single melting temperature, the heat of fusion is often assumed to be liberated on an infinitely thin surface dividing the liquid and solid regions. For a binary mixture, the heat is assumed to be uniformly released in the mushy region. These assumptions imply that the length scale for the solidification zone is much smaller than those for heat and mass diffusion.

When a small solid region spontaneously forms in its own melt without the aid of foreign materials, it is said to nucleate homogeneously. In practice, even the purest samples contain a finite number of impurity particles. When these particles initiate solidification, the large thermodynamic barrier associated with homogeneous nucleation is avoided.[1,3] Consequently, heterogeneous nucleation occurs at temperatures well above those for homogeneous nucleation.

Using clean samples in controlled environments, it is possible to cool a liquid below its equilibrium melting temperature without solidification occurring. This thermal supercooling, or undercooling, is generally limited by the presence of heterogeneous nucleation sites. Another type of undercooling is known as constitutional supercooling. The actual temperature, away from the

interface, is governed by heat flow and, in general, will not equal the equilibrium liquidus value at any given location. If, in fact, the temperature is lower than the liquidus temperature, the material is said to be constitutionally supercooled. Thus, in several situations it is possible for phase changes to occur at temperatures other than the equilibrium temperature.

As initial undercooling and rate of heat extraction increase, solidification interface speeds increase and the deviation from equilibrium is larger. Eventually, the assumption of local equilibrium at the interface is no longer valid. Typically in past modeling, this assumption was replaced with 'response functions' which might relate interface velocity and composition to local conditions, such as undercooling, crystal growth orientation and interface curvature[6]. Turnbull[9] and Cahn *et al.*[2] proposed empirical relations between these variables. These were often based on experiments which used the physical structure of small material samples to relate overall cooling rates and interface velocities to known amounts of initial undercooling.

Much of the mathematical difficulty with finding solutions to phase change problems stems from three causes. First, the problems are non-linear, so that superposition is not applicable and each case must be treated separately.[4,7] Another difficulty, which is actually a distinguishing characteristic of phase change problems, is that the transition interface moves. Since its location is not known a priori, it must be determined as part of the solution. In mathematical terms, these are free boundary value problems, or Stefan problems. Finally, any significant density difference between the phases requires the addition of a convective term in the governing energy equation.

In spite of these difficulties, progress has been made in the solution of these problems, in particular those for which equilibrium assumptions are invoked. Exact, analytical solutions exist only for a limited number of equilibrium phase change problems and these are limited to idealized situations with simple boundary conditions.

Further progress has been made using various approximate analytical methods, such as the integral method, which is useful for non-linear problems. Asymptotic methods have also proven valuable in the solution of phase change problems by exploiting the presence of large or small parameters appearing in the dimensionless formulation of problems. These parameters might include, for example, slight relative density differences between the solid and liquid regions, or the Biot number.

For more complicated problems, investigators have turned to numerical methods. Often, enthalpy is used as the major dependent variable and the temperature distribution is later extracted from a temperature-enthalpy relation. In this formulation the interface location is eliminated from the calculations, so it can handle pure substances as easily as binary systems.[8] Numerical methods are also used to solve non-equilibrium solidification problems where response functions are employed at the interface.

C.3. **Objective**

The objective of this research is to use first principles to predict solidification rates and solidification zone structure in terms of parameters appearing in the nucleation kinetics laws and governing energy equation. Clearly, to understand the solidification zone, it is necessary to include the nucleation process in the mathematical models and examine length scales on the order of the solidification zone. This coupling of the nucleation rate laws and the continuum equations will describe heat release as a function of temperature, composition and material properties.

C.4. **Problem Formulation**

To illustrate a conventional solidification model, consider the most elementary situation possible, that is, the planar solidification of a pure material. Within the solid and liquid regions, the assumptions of constant and uniform density, thermal conductivity and heat capacity, and negligible dissipation and compressibility effects, reduce the energy equation to a balance of heat conduction

and temporal changes in energy. At the interface, an energy balance between heat of fusion released and heat conducted into the solid and liquid regions is combined with mass conservation. The resulting expression relates temperature gradients, material properties, and the interface velocity.

This condition tacitly assumes that the solidification surface is infinitely thin. Assuming local equilibrium, a second interface condition is that the solid and liquid interface temperatures have the value T_m, the equilibrium melting temperature.

At the external surface of a finite material region, a variety of boundary conditions are possible, such as specified temperature or heat flux, or heat losses due to convection or radiation. If dealing with an infinite material, conditions at infinity must be prescribed.

The above formulation typifies traditional solidification models in which the structure and kinetics of the transformation region are hidden. To illustrate the approach incorporating interface structure, consider the solidification of a subcooled pure liquid. Again, the most elementary model is described. The homogeneous nucleation rate per unit volume, N, may be represented by an Arrhenius-type equation, $N = A \exp(-Q/KT)$, where Q is an activation energy, K is Boltzmann's constant and the pre-exponential factor, A, depends upon the shape and size of the nucleus.[1,3,5,10] The heterogeneous nucleation rate may also be represented by the same type of expression, but with different pre-exponential and activation energy terms.[3] Since Q may be a function of temperature, there is often a maximum in the nucleation rate occurring at some temperature below T_m.

The concept of dynamic equilibrium of atoms passing between the liquid and solid regions leads to $R = B (T_m - T)$, an approximate relation between the growth rate or speed, R, of the nuclei surfaces and the amount of subcooling.[3,9] The parameter B depends mainly upon material properties. This is reasonable for non-viscous liquid metals with mass diffusion coefficients which are reasonably insensitive to temperature.[3,9]

To complete the problem formulation, an additional term representing the heat of fusion released due to nucleation must appear in the governing energy equation as a source term. The resulting equation is valid throughout the solid, liquid and transformation regions, although the various terms will be of different relative sizes in the different regions. The nucleation heat generation rate per unit volume, q, may be written as $q = Dh(df/dt)$, where D is the density, h is the specific heat of fusion and f is the volume fraction of transformed material which may be expressed as $f = 1 - \exp(-at^n)$.[1,10] The parameters a and n are constants depending mainly upon nucleus shape and material properties.[1,10] The above expression for volume fraction has been corrected for the fact that the fractions of transformed and untransformed material sum to unity and that the transformed material is no longer able to support nucleation.

C.5. Conclusion

Conceptually, the rapid solidification problem is analogous to current combustion theory for flames and detonations. They have in common the ideas of a relatively thin reaction zone supporting a rapid, temperature dependent transformation, Arrhenius-type kinetic laws, and 'species' conservation. The resulting equations are similar. Thus, it may be possible to apply some of the perturbation and numerical solution techniques which have been successful in combustion modeling.

The problems in this project center on understanding and predicting rapid solidification and solidification of undercooled melts. Past attempts to account for these phenomena used empirical expressions, relating interface velocities to local undercooling, in place of the equilibrium free boundary conditions. This work departs from those ideas by including the important physics of nucleation and heat release, thereby giving the solidification region some structure.

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D. COMPUTER-AIDED ANALYSIS OF FLOW, TRANSPORT AND STABILITY OF SYSTEMS WITH FREE AND/OR MOVING INTERFACES

R.L. Sani, Professor, Department of Chemical Engineering
E. Crespo del Arco, Visiting Professor, Research Associate, CLgFT
A. Alshamlan, Graduate Student, Chemical Engineering Department

D.1. Introduction

There are many terrestrial and low-g processes in which a free and/or moving surface plays a dominant role in the dynamics of the system. In general, examples abound in static and dynamic capillarity, bubble dynamics, electrochemical corrosion and etching, separation science, material science and many other areas. While the modeling of such systems has accelerated recently, progress has been slowed by the complexity and inherent nonlinearity of realistic systems as well as the necessity of well-defined associated physical experiments for validation. In particular in the modeling problem, one of the limitations has been the imposition of two dimensionality, or axisymmetry[4,12,25], and, in some cases, neglect of convective transport[4] and/or a fixed domain shape[12]. This raises the question of whether even the most sophisticated of these models is capable of predicting the dynamics of a physical system since, for example, three dimensionality and/or deformability effects may play a significant role.

The modeling effort and associated development of state-of-the-art computational tools described herein is focused on extending a state-of-the-art model with very general free surface capability to include the assessment of the linear stability of the system to *three-dimensional perturbations*. While, in general, the full three-dimensional simulation of these complicated systems

is not feasible even in today's supercomputing world, the linear stability assessment can be done and, in fact, we believe is logical next step beyond two-dimensional simulations.

D.2 Relevance of Project

The information obtained from such an analysis leads to insight into the fundamental flow and transport mechanisms controlling the system and can be used to predict appropriate operating windows and to determine control strategies for the process. In addition, a weakly nonlinear analysis can be formulated utilizing the linear stability results and is capable of modeling system behavior in regions of parameter space where both full numerical models, as well as physical experiments, may be very difficult to perform[10,20,25,26]. (See, for example, the contribution of Hardin and Sani in Appendix I: Research Related Reports, that utilizes a similar weakly nonlinear analysis.)

While the modeling effort described herein is applicable to not only the general class of free and/or moving interface systems mentioned previously but also to fixed boundary systems, the focus of our current low-g research is on the flow, transport and stability of floating zones and bubbles in which thermocapillary and diffuso-capillary effects are included. Floating zone processes are important in the growth of high purity silicon and other high temperature materials and is being considered as a viable low-g process for other systems. There have been several flight experiments that have addressed the behavior and shape of passive float zones (FSLP, Spacelab 1; FLIZ; Spacelab D1 Mission) and active float zones (Texas flights 3, 7, 9,10; Spacelab 1, STS 41-D) and several proposed for future missions[16,18,21,25].

Bubble dynamics are important in many aspects of separation and material sciences in a low-g as well as a terrestrial environment. The migration of bubbles, or drops, plays an important role in many engineering science and space manufacturing problems[7,11,13,21]. In material science processes such as the manufacturing of glasses, etc. gas bubbles can be formed from the byproducts of chemical reactions or gas trapped in the interstices of the raw material[15]. In the low g-environment of space, forces other than gravitational must be utilized as a bubble separation technique. It is well known that gradients in interfacial tension on the bubbles' surface can promote droplet motion in the direction of decreasing interfacial tension and hence provide such a separation mechanism[9,15]. Thus, the role of thermocapillary and diffusocapillary migration of a bubble, or drop, can be of paramount interest in material processing in space.

Consequently, after addressing our primary focus, floating zones, we plan to use the *same* numerical model to address such bubble migration related issues as (1) the effect of surfactant, (2) the effect of deformation, (3) convective transport effects, (4) multiple bubble effects and (5) any convective instabilities associated with the bubble system[28]. This latter study will reinforce the previous two Center projects, could provide a modeling resource for related NASA Center projects and will be the foundation of a Ph.D. dissertation in a low-gravity related area.

Finally again focusing on our first initiative, floating zones, it is noteworthy that concurrent with the design of new flight experiments involving floating zones is the design of flight furnaces appropriate for floating zone processing. The modeling proposed herein will provide some useful data for experiment design and furnace design. It will also provide fundamental insight into the interplay among the various physical mechanisms which drive the system and trigger instabilities; in fact, one of the most exciting aspects of this study will be the assessment and understanding of these. Recently, there have been experimental observations of oscillatory convection in a reduced gravity and terrestrial environments[9,12,25], conjectures on the mechanism of the instability, and stability analyses of simpler cases. However, it appears that not even the case of the passive half-floating zone is quantitatively understood. In addition, most observations and many analyses are limited to large Prandtl number fluids (i.e. greater than 6.5), whereas most interesting electronic materials have Prandtl numbers less than 0.1. Both the determination of the point and cause of the onset of temporal and/or three-dimensional flow as well as the associated spatial structure for general Prandtl number fluids will be addressed in this research. Thus, we hope to provide the appropriate *Rayleigh stability criterion*[11] for the process and explore its dynamical behavior. In the floating zone crystal growing process these issues can be critical ones in addressing product quality. Transient flows lead

to undesirable and often nonavailable nonuniform dopant distribution; nonuniform spatial flows can likewise lead to similar undesirable dopant distribution[10]. They can also generate additional thermal and lattice stresses which can lead to catastrophic failure.

D.3 Interaction with Flight Experiments

It is essential to validate the models for such complicated systems against experimental observations to guarantee that the model is capable of predicting behavior that can be realized. This is especially true here because of the uncertainties in modeling the free and/or moving interfacial regions. In our study this will be accomplished by collaboration with other investigators who possess experimental data and/or are planning flight or terrestrial experiments. Currently, such is the case with our interactions with D. Lind and Rockwell International's FEA experiments as well as with D. Schwabe's Texas, Spacelab 1 and STAT 41-D experiments[25,26]. In addition, we will provide modeling capability in experiment design and data assessment for an international collaborative research effort proposed for IML-2 or a USML mission[29].

D.4. Formulation

The continuum model is derived from fundamental balances of mass, momentum, species and energy and is simplified by invoking the Boussinesq approximation[19]. This leads to:

$$\rho\left[\frac{\partial \boldsymbol{u}}{\partial \theta} + \boldsymbol{u}\cdot\nabla\,\boldsymbol{u}\right] = \nabla\cdot\tau - \nabla\, p + \boldsymbol{b}\,(\boldsymbol{C},T) \tag{1}$$

$$\nabla\cdot\boldsymbol{u} = 0 \tag{2}$$

$$\frac{\partial C_i}{\partial \theta} = -\nabla\cdot\boldsymbol{N}_i + R_i\,(\boldsymbol{C},T) \tag{3}$$

$$\rho C_p\,\frac{\partial T}{\partial \theta} = -\nabla\cdot\boldsymbol{q} + Q(\boldsymbol{C},T) \tag{4}$$

where

	$\mathbf{u}$	= fluid velocity
	τ	$= \frac{\mu}{2}(\nabla\,\boldsymbol{u} + (\nabla\,\boldsymbol{u})^T)$
	$\mathbf{N_i}$	$= -D_i\nabla C_i + \boldsymbol{u}\,C_i$
	$\mathbf{q}$	$= -\,k\nabla T + \rho C_p \boldsymbol{u} T$
	C_i	= concentration of species i
	T	= temperature
	p	= pressure
$R_i(\mathbf{C},\mathbf{T})$		= bulk reaction rate of species i
$Q(\mathbf{C},\mathbf{T})$		= bulk heat source term
$f(\mathbf{C},\mathbf{T})$		= gravitational body force term

In any solid phases, present equations analogous to (2) and (3) are also written. However, the fluxs $\mathbf{N_i}$ and $\mathbf{q}$ in the solid phase will only possess convective transport terms if the system is viewed from a moving frame. Hereafter C_{is} and T_s will denote, respectively, the concentration and temperature in the solid phase.

In order to complete the mathematical formulation, an appropriate set of initial and boundary conditions must be specified. The usual conditions of a specified magnitude or appropriate flux, for field variables ($\mathbf{u}$,p,T,C,) are adequate for those portions of the domain's boundary which are fixed and passive. The free and/or moving boundary portions of the domain must be addressed more carefully. As in Engelman and Sani[5], the free liquid surface boundary conditions (assuming, for example, passive vapor phase) are:

$$\frac{1}{|\nabla S|}\frac{\partial S}{\partial \theta} + \boldsymbol{u}\cdot\boldsymbol{n} = 0 \tag{5}$$

$$\boldsymbol{nn} : \boldsymbol{\tau} = -p_o + 2\sigma H \tag{6}$$

$$\boldsymbol{tn} : \boldsymbol{\tau} = 0 \tag{7}$$

$$k\boldsymbol{n}\cdot\nabla T = h(T - T_o) + Q_R(T) \tag{8}$$

where $\mathbf{n}(t)$ is a unit outward pointing surface normal (a unit surface tangent vector), T_O and p_O are, respectively, the ambient temperature and pressure, $Q_R(T)$ is a surface heat source or sink which could, for example, be radiant heat transfer, H is the mean Gaussian curvature of the interface, and $S(\mathbf{x},t) = 0$ is the free surface location.

At solid-liquid boundaries (i.e., melt interfaces), the general boundary conditions are:

$$\boldsymbol{n}\cdot(k\nabla T - k_s\nabla T_s) = \lambda\rho_s\boldsymbol{n}\cdot(\boldsymbol{u}_s - \boldsymbol{u}_i) \tag{9}$$

$$\boldsymbol{n}\cdot(D\nabla C_i - D_s\nabla C_{is}) = (K_i - 1)C_i\boldsymbol{n}\cdot(\boldsymbol{u} - \boldsymbol{u}_i) \tag{10}$$

$$T_s = T_m + mC_{is} - \Gamma H \quad , \quad T_s = T \quad , \quad C_s = kC_i \tag{11}$$

$$\rho_s\boldsymbol{n}\cdot\boldsymbol{u}_s - \rho\boldsymbol{n}\cdot\boldsymbol{u} = (\rho_s - \rho)\boldsymbol{n}\cdot\boldsymbol{u}_i \quad , \quad \boldsymbol{t}\cdot\boldsymbol{u} = 0 \tag{12}$$

where λ is the latent heat of fusion, $\mathbf{u_i}$, $\mathbf{u_S}$ and $\mathbf{u}$ are, respectively, the velocity of the interface, solid and liquid, m is the slope of the liquidus curve at T_m, the normal melting point, Γ is the capillary length, k is the distribution coefficient and $K_i \equiv (C_{is}/\rho_s)/(C_i/\rho)$. In our study we will make, at least initially, some simplifying assumptions such as neglecting specie diffusion in the solid when considering multicomponent solutions, $k_s \approx 0$, etc.

Even with the utilization of current state-of-the-art numerical techniques and hardware, one is often forced to restrict the model by imposing two dimensionality, axisymmetry and/or time independence for feasibility, or at least affordability. The assessment of such models is essential if physically realistic results are to be generated. Most steady models admit solutions which often cannot be physically realized because they are unstable under normal operating conditions[3].

A linear stability analysis is one means of making an initial assessment of the ability to realize such systems; it is proposed here to develop and incorporate one which will focus on determining the most dangerous mode when the system is subjected to two- and three-dimensional perturbations as well as determining a selected set of *next* most dangerous models. (In many cases, the perturbation in the third dimension can be effected spectrally, which reduces the problem to a pseudo two-dimensional one on the two-dimensional, or axisymmetric, spatial domain of the unperturbed system.) This will allow us to assess whether the model solution can be realized, and also will lead to some valuable insight if one must resort to a three-dimensional model; for example, whether the solution might be time-dependent and/or what are the most important spatial temporal scales.

Formally the linear stability problem is obtained by defining primed perturbation variables from a base state $u = \hat{u} + u'$, $p = \hat{p} + p'$, $T = \hat{T} + T'$, $C_i = \hat{C}_i + C_i'$, $S = \hat{S} + S'$:

$$\rho\left[\frac{\partial u'}{\partial \theta} + \hat{u}\cdot\nabla u' + u'\cdot\nabla \hat{u}\right] = \nabla\cdot\tau' - \nabla p' + b'(C', T') \tag{13}$$

$$\nabla\cdot u' = 0 \tag{14}$$

$$\rho C_p\left(\frac{\partial T'}{\partial \theta} + \hat{u}\cdot\nabla T'\right) = -\nabla\cdot q' + Q'(C', T') \tag{15}$$

$$\frac{\partial C_i'}{\partial t} + \hat{u}\cdot\nabla C_i' = -\nabla\cdot N_i' + R_i'(C', T') \tag{16}$$

plus the appropriate linearized boundary conditions. The latter are rather complicated on the free and/or moving interfaces and must be derived carefully and consistently. The derivation of the perturbed boundary conditions are presented in detailed in D.T.C. Lee[14] and S.K. Fung[7] and are omitted here in the interest of brevity.

Even in the more simple cases, the continuum model is nonlinear and, in general, the various fields couple in a complicated fashion. While analytical solutions can be generated to some limiting cases, in general a numerical solution must be used to solve not only the general base flow problem but also the associated linear stability problem.

D.5. Numerical Model

Finite difference methods (FDM) have played an essential role in the development of methods in computational physics. However, within the last ten years descretization methods such as Galerkin's technique using local polynomial basis functions, herein referred to as Galerkin-finite element method (GFEM) have become serious competitors in many cases. The GFEM method has inherently built into it the properties of being appropriate to irregularly shaped domains and of allowing the modeler to grade his "mesh" to allow for any known local structure in the solution to the problem. These properties, plus the accuracy of the GFEM methods, make it an attractive method for the simulation of free and/or moving boundary problems where determination of the domain shape is an essential part of the problem. The algorithm which will be utilized for problems involving shape changes is built around a GFEM incorporating an adaptive mesh capability. The algorithm solves the "weak form" of the appropriate mathematical model of the system[2,6].

The mesh adaptation scheme built into the algorithm allows the movement of "boundary nodes" and other "nodes" along prescribed lines in space, which themselves may be tiled automatically in order to maintain a "reasonable" mesh of elements with predetermined aspect ratios; additionally, in some cases our algorithm allows the injection of elements. These features guarantee that the accuracy of the technique is maintained as the domain shape changes. For cost-effectiveness the algorithm also allows for only parts of the computational domain to be dynamically altered during the simulation. Such a mesh adaptation technique, except for the dynamic injection of elements, has been effectively utilized in modeling related areas such as crystal growing and phase change problems[5] and coating flows[13]. The GFE and adaptive mesh technique used in this study are discussed in more detail in Engelman and Sani[6] and Kistler and Scriven[13].

The GFEM generates a coupled system of nonlinear ordinary differential equations (a nonlinear algebraic system in the case of steady problems) of the form:

$$\mathcal{M}_1\dot{U} + \mathcal{B}_1\dot{S} = \mathcal{N}_1(U)U + \mathcal{B}_1 S + \mathcal{K}_1 U + CP + F(C, T) \tag{17}$$

$$\mathcal{M}_2\dot{T} + \mathcal{B}_2\dot{S} = \mathcal{N}_2(U)T + \mathcal{B}_2 S + \mathcal{K}_2 T + Q(C, T) \tag{18}$$

$$\mathcal{M}_3\dot{C} + \mathcal{B}_3\dot{S} = \mathcal{N}_3(U)C + \mathcal{B}_3 S + \mathcal{K}_3 C + R(C, T) \tag{19}$$

$$\mathcal{M}_4\dot{S} = \mathcal{B}_4 U \tag{20}$$

$$0 = C^T U - g_1 \tag{21}$$

$$0 = \mathcal{B}_5 T - g_2 \tag{22}$$

$$0 = \mathcal{B}_6 C - g_3 \tag{23}$$

The current algorithm utilizes a skyline linear algebraic system solver which is specifically designed for matrices that are banded, but with variable band width. The technique profiles the Gaussian elimination technique into a series of vector inner product operations. Consequently, the algorithm can be vectorized for efficient computation. However, we plan to investigate two other algorithms, a vectorized frontal scheme as well as a matrix-free iteration scheme. The latter requires a pre-conditioner; at this point we are still floundering in this area. Some steady examples of both free and fixed domain simulations are included in the Progress Report in Appendix I.

The associate linear stability problem will be of the general form:

$$\mathbf{M\dot{z} = Tz} \tag{24}$$
$$\mathbf{Vz = 0} \tag{25}$$

Implicit in the matrix operators **M**, **T** and **V** are the physical and geometrical parameters that characterize the physical system that is being studied. If there exist non-trivial solutions to (12)-(13) when subjected to a random initial condition the system is said to be unstable, and in this manner one can gain some insight into the physical processes as well as an ability to predict a stable operating window.

One solution technique for (24)-(25) is a direct numerical integration which, in general, leads to the fastest growing disturbance in the unstable case. Also, the stability of the system can be assessed by successively varying an appropriate system parameter until an unstable system is obtained. This method can lead to useful results as shown in Appendix I, but it only leads to a bracketing of the point of instability and only the most dangerous mode of instability is obtained. However, this can be one of the most useful methods for base systems which are time dependent.

A second, more powerful, technique which is appropriate to steady base systems or those transient ones in which one makes a *frozen time* assumption is obtained by assuming an exponential time dependence for **z**, i.e. $\mathbf{z} = \mathbf{y}\exp(\sigma t)$. The latter leads to an algebraic eigenvalue system

$$\mathbf{Ty} = \sigma\,\mathbf{My} \tag{26}$$
$$\mathbf{Vy = 0} \tag{27}$$

and the system is (a) unstable if $\mathrm{Re}\,\sigma > 0$, (b) marginally stable if $\mathrm{Re}\,\sigma = 0$ and (c) stable if $\mathrm{Re}\,\sigma < 0$. Solving this problem leads to not only a linear stability window for the process, but also all the characteristic modes for the system, i.e. the spatial structure of the modes, as well as the associate frequency of any oscillatory temporal behavior.

In the numerical modeling of such complicated systems as being addressed herein one requires a large number of degrees of freedom to adequately track the physics of the process. This means the size of the system (26)-(27) will, in general, be very large. In addition, since we are subjecting the process to three-dimensional disturbances the system implicitly contains a parameter, say α , which characterizes the wavelength of the disturbance in the third dimension, i.e. the dimension not included in the original two dimensional domain, and one must seek the most dangerous value of α by a search technique which requires multiple solutions of the algebraic eigenvalue problems. Consequently, for cost effectiveness, or even for feasibility in some cases, an iterative scheme will be used to solve for a selected number of most dangerous modes of the eigenvalue problem[16,17].

Since the matrix eigenvalue problem is very large and nonsymmetric, the problem of algorithm selection become a crucial issues. While there exist library subroutines, for example, in ISML or EISPACK, for this purpose these are not cost effective for solving our large unsymmetric system, especially since only a limited number of most dangerous modes are of interest. Here an iterative scheme based on Arnoldi's subspace method with deflation [1,22,26] will be implemented. Our initial use of this method also showed that the initial guess could be effectively preconditioned by actually integrating the system for a "long enough time" so that decaying modes could be sufficiently suppressed. In our current scheme such a preconditioning scheme will be implemented along with an appropriate eigenvalue shifting transformation in order to focus the algorithm on the most dangerous modes. We will, as well, incorporate a Chebychev acceleration of the subspace iteration scheme. In this manner we hope to develop an efficient iterative scheme for these and other problems.

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